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Optimization of coprecipitation using response surface methodology in combination with experimental design for determination of trace Ni by flame atomic absorption spectrometry in biodiesel produced from waste cooking oil

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In this study, the Box-Behnken design (BBD) of the response surface methodology (RSM) has been used to optimize the coprecipitation variables (coprecipitation pH, Al:Ni mole ratio, injection speed of base) for preconcentation of Ni using aluminum hydroxide to obtain accurate quantitation of Ni in biodiesel samples produced from waste cooking oil (WCO) by homemade flame atomic absorption spectrometer. The performance of homemade flame atomic absorption spectrometer has been evaluated through comparison with Perkin-Elmer 5100 PC flame atomic absorption spectrometer using aqueous standard solution of Cu, Ni. The predicted optimal conditions of statistical are pH=10.5 and Al:Ni mole ratio of 1.96×10^4, while the injection speed for NaOH is 0.85 mL/min at the concentration of 1.0 mol/L. The concentration of Ni is μg/L level and preconcentration factors is between 50~200. To assess the accuracy of purposed method, a recovery test has been performed and compared to analytical values of Perkin-Elmer 5100 PC GFAAS.

Keywords: Biodiesel, Box-Behnken, Coprecipitation, Flame atomic absorption spectrometer, Quantitation of Ni, Response surface methodology, Waste cooking oil

Introduction

The ever increase in global energy demand, consumption of depletable fossil fuels, exhaust emissions and global warming, all of which led to search for alternative fuels. Biodiesel is presented as a natural substitute of diesel, being a renewable, biodegradable and non-toxic fuel derived from biological sources such as vegetable oil or animal fat[1,2]. The use of biodiesel fuel presents better lubricity, higher viscosity and lower emission of carbon monoxide, carbon dioxide, sulfur dioxide and hydrocarbons than that of diesel fuel[3-5]. Trace amounts of toxic elements As, Cd, Hg, Pb and heavy metals Fe, Mn, Ni, V, Cu are released into the environment due to combustion of fuel in automobiles which are important sources of atmospheric pollution[6-8]. Metals and other elements in biodiesel may come from natural sources of the soil and atmosphere where the vegetable plant or grain crops are grown. On the other hand, heavy metals may come with trace amounts from the extraction of oil or fat, the synthesis (from catalysts), washing, refining, transportation and storage for producing the biodiesel. Recently, "green diesel" has been produced from transesterification with ethanol, methanol in the existence of catalysts based on alkali, alkaline-earth metals or from hydrocracking reactions catalyzed with Ni in order to eliminate unsaturated bond components of polyunsaturated ester in waste cooking oil (WCO)[9-14]. Catalysts based on metals including Ni, are good hydrogen adsorbers and low-cost, so various catalysts such as Ni-impregnated zeolites, activated carbon supported NiP, NiO which is coated on Al_2O_3 have been used to produce biodiesel[15-19]. The production of biodiesel using catalysts inevitably involves the trace amounts of heavy metals into the fuel.

Although heavy metals such as Ni, Mn, Cu, Fe and V exist at low concentration in biodiesel, but they may catalyze the oxidation process of fuels and contribute to failure of the fuel filter due to clogging and corrosion of burner exhaust pipes from deposition in their oxides after combustion[20,21]. Especially, Ni and V contribute greatly to fuel pump, engine piston and piston ring wear besides the engine deposits in the fuel system. The content of Ni in liquid fuels including petroleum, diesel, bioethanol and biodiesel plays an importance role to estimate the quality of fuel.

Many Atomic spectrometric techniques have been used to determine the quantity of metals in biodiesel

such as flame and graphite furnace atomic absorption spectrometer, inductively coupled plasma atomic emission spectrometer, inductively coupled plasma-mass spectrometer and wavelength dispersive X-ray fluorescence spectrometer, etc.[22-28]. Methods of dilution with organic solvents tetramethylammonium hydroxide and ethanol were used to analyze the biofuel in graphite furnace atomic absorption spectrometry and inductively coupled plasma-mass spectrometry with high sensitivity and wide linear range. These analytical methods are not widely used in the general laboratory due to their high costs.

The common availability of the instrumentation, simplicity of the procedure, speed, high precision and accuracy of the technique still make flame atomic absorption method an attractive alternative. However, flame atomic absorption spectrometry (FAAS), suffers from insufficient sensitivity for the direct determination of metal ions in environmental samples, biodiesel productions. In order to overcome this problem, various extraction methods have been reported that improved concentration factor including solid-phase extraction, liquid-liquid extraction, and microemulsion breaking extraction[29-31]. The concentration factors of extraction methods using organic solvents almost is only between 50~80, and the effects of waste from organic solvents impact into environment.

From this perspective, methods by inorganic materials have been developed in parallel extractions. Main advantage of concentration with inorganic materials is low-analytical costs and low-effects to environment. Concentration method using Fe_3O_4 nanoparticles was also investigated [32]. Coprecipitation is one of the methods that uses inorganic materials. $Al(OH)_3$ is readily available, inexpensive and relatively non-toxic in comparison to many other metal hydroxide coprecipitants.

This study describes the optimization and validation of coprecipitation with $Al(OH)_3$ + FAAS method for analysis of Ni using response surface methodology (RSM). This facilitates the optimization step of experimental conditions which is a very complex step because of the large number of parameters that must be simultaneously tested. RSM is a group of mathematical and statistical techniques that are used for improving and optimizing analytical methods and are commonly used to get the best experimental parameters for determination of chemical components. Optimizing of coprecipitation using a conventional "change-one-factor-at-a-time" process is very time-consuming, and, moreover, this method may not find the true optimum since interactions between experimental variables are neglected. On the other hand, experimental design based on statistical modeling can be a very useful tool to evaluate the interactions between a set of independent experimental factors and observed responses, and, moreover, is a time saving method since it requires the least number of experiments[33-36].

Quantitative analysis of trace Nickel in biodiesel produced from waste cooking ioil (WCO) using Ni catalysts with optimized experimental parameters from RSM and homemade instrument was investigated. The utility was estimated through comparison with Perkin-Elmer 5100 PC flame atomic absorption spectrometer.

Experimental Section

Reagents and Samples

Analytical grade of chemical reagents including $Al(NO_3)_3 \cdot 3H_2O$, KCl, NaOH, HNO_3, H_2SO_4, HCl etc. (Tianjin, China) and deionized water were used throughout the experimental work. Standard solutions of the Cu, Ni were prepared by diluting aqueous stock solution of 1000.0mg/L (Shanghai, China). Before use all of the glassware were washed with deionized water and dried. Four samples of different WCOs were obtained from various restaurants.

Instrumentation

Perkin-Elmer model 5100 PC flame atomic absorption spectrometer was used to estimate homemade instrument. Perkin-Elmer model 5100 PC graphite furnace atomic absorption spectrometer was used to confirm the analytical results of real samples. The homemade spectrometer was equipped with a ruled diffraction grating as a dispersion element which has 1800 lines/mm, blaze wavelength of 230 nm, size of 50 mm^2, Hamamatus R-928 photomultiplier tube (PMT) as a detector, a Czerney-Tuner monochromator with focal length of 450 mm, air-acetylene pre-mix burner with a length of 10 cm long and deuterium background correction. Nickel hollow cathode lamp was used as light source at wavelength of 232.0 nm. The operating parameters of element were set according to the manufacturer recommendations. Thermo Orion 3 stars digital pH meter was used for measuring all solutions and Sorvall LYNX 4000 centrifuge was used for sorting out precipitations from solutions. Minitab-17(Minitab, Inc., State College, PA, USA) was employed for analysis of data and experimental design[37].

Performance check of homemade FAAS

To estimate the performance of homemade FAAS, characteristic concentration (1% absorption) of Cu and characteristic concentration, characteristic concentration check value and the linear range of Ni was determined. The characteristic concentration check value is the concentration of element (in mg/L) that will produce a signal of approximately 0.2 absorbance unit under optimum conditions that wavelength listed. The indices of homemade and Perkin-Elmer 5100 PC FAAS are showed in Table 1. As seen in Table 1, the performance of homemade FAAS was similar to Perkin-Elmer 5100 PC FAAS.

Pretreatment of samples

Hydro-pyrolysis of the four WCOs was carried out to produce biodiesel. First, food dreg was eliminated from WCO by filtrating through a normal sieve, followed by removing water present by heating at 100℃ for 10 min. 500 mL of the samples were put into the batch reactors respectively and 0.25 g of the activated NiO/SiO_2 catalyst was added using catalyst holder, followed by N_2 gas was used to purge the reactors for 2 min in order to have an inert atmosphere. H_2 was introduced into the reactors until the pressure reached 0.5 MPa and the systems were sealed and then heated to 300℃ for 3h. The reactors were cooled and separated biodiesels.

A mass of approximately 1.0 g of obtained samples were weighed respectively and directly into a digestion tube, and then 2.0 mL of H_2SO_4 and 2.0 mL of concentrated HNO_3 were added. Then the samples were heated and held at 150℃ for 2 h. Then more 2.0 mL of concentrated HNO_3 were added and mixture was heated and held at 180℃ for 2 h. Finally, an aliquot of 2.0 mL of 30% (w/w) H_2O_2 was added to the medium. The obtained clear solution was then cooled to room temperature and transferred to a 25 mL volumetric flask. The total volume was diluted to 25 mL with ultrapure water.

Preconcentration of Ni

1.0 mL of 1.0 mol/L $Al(NO_3)_3$ solution was put into sample solutions having a volume of 25 mL and the mixtures were stirred while adding 1.0 mol/L NaOH using a peristaltic pump. After coprecipitation, precipitations were separated from mixtures by centrifuging at the speed of 6000 rpm for 2 min. Then precipitations were dissolved with 20 µL of 20%(v/v) HNO_3 and then 10%(w/v) KCl solutions were added as an ionization buffer. To adjust the volume of sample solutions to 25 mL/factor of preconcentration, deionized water was used. A brief explanation of the above-mentioned steps is represented in solutions of blank and Ni standard to prepare the concentration solutions. In general, just like blank solutions above-mentioned contain about 30 metal elements at high contents (g/L or mg/L) including Na, Ca, K, Mg, Cu, Fe etc. The prepared solutions of samples and standards were injected with microinjection system to flame or graphite furnace atomic absorption spectrometers.

Experimental design for Ni recovery optimization

Response surface methodology (RSM) with Box-Behnken Design (BBD) was applied in this experiment to determine the optimum condition for preconcentration of Ni.

The critical parameters and their levels (low and high) for the experimental design were determined through preliminary experiments. The following parameters were examined in this step: coprecipitation pH, Al:Ni mole ratio (*X2*), stand time, concentration of base, injection speed of base, preconcentration factor, concentration of Ni^{2+}. Base on the preliminary results, three independent factors: coprecipitation pH(*X1*), Al:Ni mole ratio(*X2*), injection speed of base(*X3*) were selected and each factor was investigated on a three-level (high +1, center point 0, low -1) as shown in Table 2.

A series of experiments were performed with Ni concentrations of 0.4 and 2.0 µg/L with preconcentration factor of 200 and 50, respectively. Herein, the solutions that contain wet ashed waste cooking oils were used to blank solutions. BBD design with five repeated runs at the center point of 17 trials with different combinations was optimized to obtain the response. RSM was applied to optimize the factors that influence the recovery of Ni.

Table 1 — Performance of Homemade and Perkin Elmer 5100 PC

Element	Measurement values	Homemade FAAS (mg/L)	Perkin-Elmer 5100 PC FAAS (mg/L)
	Characteristic concentration	0.08	0.14
Ni	Characteristic concentration check value	2.0	7.0
	Linear range	0.08~5.0	0.0~2.5
Cu	Characteristic concentration	0.05	0.077

Table 2 — Box-Behnken Design for the preconcentration of Ni

Variables	Factor Level		
	-1	0	+1
coprecipitation pH(X1)	5	9	13
Al:Ni mole ratio(X2)	4.9×10^3	1.19×10^4	1.96×10^4
injection speed of base(mL/min, X3)	0.1	0.8	1.5

Table 3 — Box-Behnken experimental design with three independent variables

Run No	Coded variables levels			Recovery percentage	
	X1	X2	X3	Experiment	Predicted
1	0	-1	1	55.8	58.8882
2	1	0	1	66.4	65.8854
3	-1	0	1	12.2	12.2054
4	0	-1	-1	53.2	58.8910
5	1	-1	0	58.4	56.4060
6	0	0	0	79.2	77.8848
7	0	0	0	79.4	77.8848
8	-1	0	-1	18.3	16.3074
9	0	1	-1	86.3	85.3174
10	-1	1	0	29.8	33.2516
11	1	0	-1	64.3	61.7890
12	0	0	0	79.5	77.8848
13	1	1	0	77.5	82.8324
14	0	1	1	87.7	85.3146
15	-1	-1	0	8.2	6.8252
16	0	0	0	78.4	77.8848
17	0	0	0	77.9	77.8848

Results and Discussion

Determination of Ni

The mixture of 20 µg of 20%(v/v) HNO_3 and 20 µL of 10%(w/v) KCl and wet ashed waste cooking oils that had complicated matrix and not detected Ni, which was diluted to desired volume, was used as blank solution for analysis of Ni. Despite the artificial blank solutions that are available, real blank solutions were used for more accurate optimum conditions. Homemade FAAS was used with the 232.0 nm analytical line of Ni, slit width 0.2nm, hollow cathode lamp current 5 mA.

Predicted model and statistical analysis

An experiment with 17 runs was conducted to optimize the input variables. The effect of the input variables on the recovery of Ni is shown in Table 3.

By applying multiple regression analysis to the experimental data, the response and the variable can be correlated using the second-order polynominal Eq. (1).

$$Y= -167.4 + 42.80\,X1 + 1.716\,X2 + 12.29\,X3 - 2.066\,X1^2 - 11.80\,X3^2 + 0.732\,X1X3 \quad \ldots (1)$$

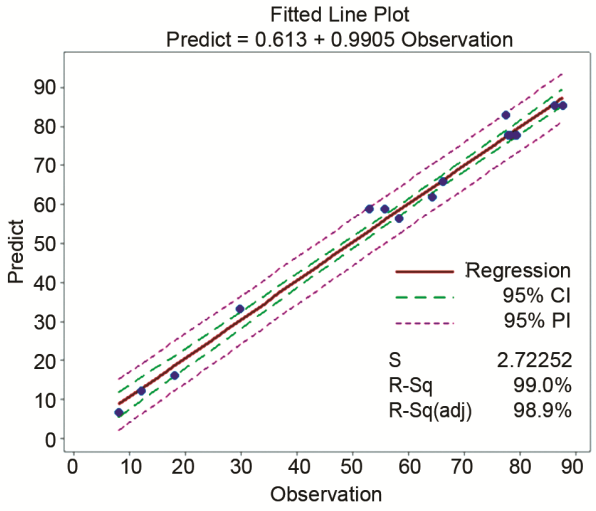

Fig. 1 — Regression plot between observed and predicted values

Here *X1*, *X2* and *X3* are the coded values of variables. The correlation coefficient (R^2=0.9901) indicated a high degree of correlation between observed and predicted values. (Fig. 1)

Table 4 shows the statistical analysis of the regression result. The model and terms are significant when the probability P-value is less than 0.05. The

R-sq and R-sq(adj) values for the regression models were both within the acceptable limits that help in the estimation of model predictive power and show that the model is a good fit with polynominal equation. Furthermore, the p-values for lack-of-fit commonly used to confirm that the model apparently represents the experimental results at a confidence limit of 95% are shown in Table 5.

Table 4 — Analysis of variance results for the model

Source of variation	Full quadratic models Recovery response p-value
Constant	0.000
pH	0.000
Al:Ni	0.000
Speed	0.014
pH*pH	0.000
Speed*Speed	0.005
pH*Speed	0.025
Residual error	
Lack of fit	0.002

Table 5 — Models fitting results

Model term	Recovery response
R-squard	99.01
Adjusted R-squard	98.41
Predicted R-squard	96.33
P-value of lack of fit	0.002

Response surface methodology (RSM)

The interaction of the input variables and the optimal level of each variable were observed by plotting them in the response surface curve. The three-dimensional response surface plots were obtained by plotting the response (Ni recovery) on the Z-axis against two input variables on X and Y axis while keeping the third variables at their "0" level.

Fig. 2(a) and Fig. 3(a) showed the effect of coprecipitation pH, Al:Ni mole ratio, and their interaction on the recovery of Ni when the when the injection speed of base was fixed at 0.8 mL/min. The recovery was maximum when the pH increased from 6 to about 9~10 and then decreased above pH 10 and was increased at high mole ratio.

Likewise, Fig. 2(b) and Fig. 3(b) showed the effect of coprecipitation pH and the injection speed of base on the Ni recovery when the Al:Ni mole ratio was fixed at 1.19×10^4. The recovery was maximum when the pH increased from 6 to about 9~10 and then decreased above pH 10 and was maximum in the range of 0.5~1.0mL/min for base injection speed. As shown in Fig. 2(c) and Fig. 3(c), the Al:Ni mole ratio positively affected Ni recovery when the speed of base was 0.9.

The optimum condition ($X1$=10.5, $X2$=1.96×10^4, $X3$=0.85) for the recovery of Ni was estimated by

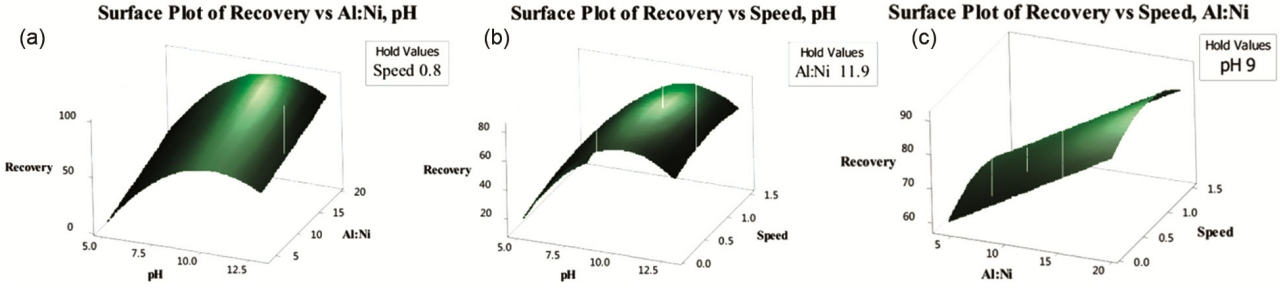

Fig. 2 — 3D-response surface plots showing the effect of (a) pH and Al:Ni, (b) pH and speed of base injection and (c) Al:Ni and speed of base injection on recovery Ni

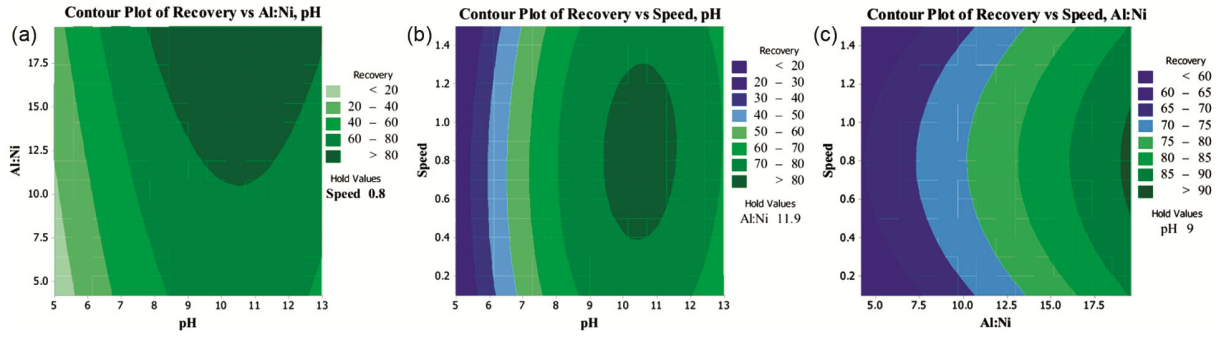

Fig. 3 — Contour plots showing the effect of (a) pH and Al:Ni, (b) pH and speed of base injection and (c) Al:Ni and speed of base injection on recovery Ni

Table 6 — Results from the determination of Ni in 4 biodiesel samples

Sample	Ni found/mgL^{-1}(mean±standard deviation, n=5)			
	Direct FAAS	Preconcentration factor	Coprecipitation then FAAS	Direct GFAAS/10^{-3}
Biodiesel 1	Not Detected	50	0.8±0.09	18.5±0.7
Biodiesel 2	Not Detected	120	2.1±0.05	19.1±0.3
Biodiesel 3	Not Detected	150	1.7±0.05	10.4±0.5
Biodiesel 4	Not Detected	200	2.5±0.1	13.2±0.9

solving the regression equation and analyzing the response surface. The theoretical recovery under the above condition was 95.5%. Under the above optimum conditions, the experimental recovery for preconcentration of Ni was obtained as 96.3%.

Analytical features of the proposed method and application

The range of standard calibration, LOQ value with preconcentration are obtain by dividing these values by preconcentration factor. The validation of the precision was performed in terms of the repeatability of 0.4 and 2.0 µg/L Ni standard solutions. The relative standard deviations and relative error were 3.3% and 4.9 for 0.2 µg/L solution, 1.8% and 2.5% for 2.0 µg/L solution. The proposed analysis method using homemade analyzer with optimal conditions for coprecipitation was employed for the determination trace Ni in biodiesel samples produced from various waste cooking oils. The accuracy was evaluated by comparing preconcentation FAAS method using homemade analyzer with direct GFAAS using Perkin Elmer 5100 PC (Table 6). From the analysis of a paired t-test was 1.73, t-stat<t-critical=2.353, the overall results for the two analyses were not significantly different at the 95% confidence level.

Conclusion

In our study, an effective experimental design was employed for optimization of preconcentration Ni in biodiesel produced from WCO by coprecipitaion with $Al(OH)_3$. The optimized experimental parameters: coprecipitation pH=10.5, Al:Ni mole ratio=1.96×10^4, speed of injection for 0.1 mol/L NaOH=0.85 mL/min. The proposed method offers a low-cost and more accurate preconcentation technique in complicated matrix samples such as biodiesels. The optimized method has low environmental effects by using inexpensive and non-toxic inorganic precipitates and simplicity, high precision and accuracy in terms of using FAAS. The result from this method and GFAAS were not significantly different at the 95% confidence interval. In conclusion, the Ni contents at µg/L levels in different biodiesel can be determined easily.

Conflict of interest

The authors declare no conflict of interest.

References

1 Sanchez-Arreola E, Martin-Torres G, Lozada-Ramírez J D, Hernandez L R, Bandala-Gonzalez E R & Bach H, Biodiesel production and de-oiled seed cake nutritional values of a Mexican edible Jatropha curcas, *Renew Energy*, 76 (2015) 143.

2 Serdari A, Fragioudakis K, Teas C, Zannikos F, Stournas S & Lois E, Effect of biodiesel addition to diesel fuel on engine performance and emissions, *J Prop Power*, 15 (1999) 224.

3 Strecker B, Hausmann A & Depcik C, Well to wheels energy and emissions analysis of a recycled 1974 VW Super Beetle converted into a plug-in series hybrid electric vehicle, *J Clean Prod*, 68 (2014) 93. https://doi.org/10.1016/J.JCLEPRO.2013.04.030

4 Kusumaningtyas R D, Normaliza N, Anisa E D N, Prasetiawan H, Hartanto D, Veny H, Hamzah F & Rodhi M N M, Synthesis of biodiesel via transesterification reaction of calophyllum inophyllum seed oil and ethyl acetate over lipase catalyst: Experimental and surface response methodology analysis, *Energies*, 15 (2022) 7737.

5 Chaves E S, Santos E J, Araujo R G O, Oliveira J V, Frescura V L & Curtius A, Metals and phosphorus determination in vegetable seeds used in the production of biodiesel by ICP OES and ICP-MS, *Microchem J*, 96 (2010) 71.

6 Uzun A, Soylak M & Elci L, Preconcentration and separation with Amberlite XAD-4 resin; determination of Cu, Pb, Ni, Cd and Bi at trace levels in waste water samples by flame atomic absorption spectrometry, *Talanta*, 54 (2001) 197.

7 Duran C, Gundogdu A, Bulut V N, Soylak M, Elci L, Senturk H B & Tufekci M, Solid-phase extraction of Mn(II), Co(II), Ni(II), Cu(II), Cd(II) and Pb(II) ions from environmental samples by flame atomic absorption spectrometry (FAAS), *J Hazard Mater*, 146 (2007) 347.

8 Lobo F A, Goveia D, Rosa A H, Oliveira A P, Pereira-Filho E R, Fraceto L F, Filho N L D & Rosa A H, Comparison of the univariate and multivariate methods in the optimization of experimental conditions for determining Pb, Cu, Ni and Cd in biodiesel by GFAAS, *Fuel*, 88 (2009) 1907.

9 Chaves E S, Lepri F G, Silva J S A, Quadros P C, Saint'pierre T D & Curius A J, Determination of Co, Cu, Fe, Mn, Ni and V in diesel and biodiesel samples by ETS-ISP-MS, *J Environ Monit*, 10 (2008) 1211.

10 Arzamendi G, Arguinãrena E, Campo I, Zabala S & Gandiá L M, Alkaline and alkaline-earth metals compounds as catalysts for the methanolysis of sunflower oil, *Catal Today*, 133 (2008) 305.

11 Lopez D E, Goodwin J J G, Bruce D A & Lotero E, Tansesterification of triacetin with methanol on solid acid and base catalysts, *Appl Catal*, 295 (2005) 97.

12 Silva R B, Neto A F L, Santos L S S, Lima J R O, Chaves M H, Santos J J R, Lima G M, Moura E M & Moura C V R, Catalysts of Cu(II) and Co(II) ions adsorbed in chitos used in transesterification of soy bean and babassu oils-A new route for biodiesel synthesis, *Bioresour Technol*, 99 (2008) 6793.

13 Thubkhun N & Tangtreamjitmun N, Determination of nickel by flame atomic absorption spectrometry after preconcentration by coprecipitation with aluminum hydroxide, *Anal Sci*, 34 (2018) 849.

14 Antakli S, Sarkis N & Al-Check A M, Determination of copper, iron, manganese, nickel and zinc in tea leaf consumed in Syria by flame atomic absorption spectrometry after microwave digestion, *Asian J Chem*, 23 (2011) 3268.

15 Wang F, Xu J, Jiang J, Liu P, Li F, Ye J & Zhou M, Hydrotreatment of vegetable oil for green diesel over activated carbon supported molybdenum carbide catalyst, *Fuel*, 216 (2018) 738.

16 Susi E P, Wijaya K, Wangsa, Pratika R A & Hariani P L, Effect of nickel concentration in natural zeolite as catalyst in hydrocracking process of used cooking oil, *Asian J Chem*, 32 (2020) 2773.

17 Kaengsilalai A, Luengnaruemitchai A, Jitkarnka S & Wongkasemjit S, Potential of Ni supported on KH zeolite catalysts for carbon dioxide reforming of methane, *J Power Sources*, 165 (2007) 347.

18 Chen L D, Wang X S, Guo X W, Guo H C, Liu H & Chen Y Y, In situ nanocrystalline HZSM-5 zeolites encaged heteropoly acid $H_3PMo_{12}O_{40}$ and Ni catalyst for hydroconversion of n-octane, *Chem Eng Sci*, 62 (2007) 4469.

19 Guo C, Rao K T V, Yuan Z, He S, Rohani S & Xu C, Hydrodeoxygenation of fast pyrolysis oil with novel activated carbon-supported NiP and CoP catalysts, *Chem Eng Sci*, 178 (2017) 248.

20 Cassella R J, Brum D M, Robaina N F, Rocha A A & Lima C F, Extraction induced by emulsion breaking for metals determination in dieseloil by ICP-MS, *J Anal Atom Spectrom*, 27 (2012) 364.

21 Cassella R J, Brum D M, Lima C F, Caldas L F S & de Paula C E R, Multivariate optimization of the determination of zinc in diesel oil employing a novel extraction strategy based on emulsion breaking, *Anal Chim Acta*, 690 (2011) 79.

22 Cassella R J, Brum D M, de Paula C E R & Lima C F, Extraction induced by emulsion breaking: a novel strategy for the trace metals determination in diesel oil samples by electrothermal atomic absorption spectrometry, *J Anal Atom Spectrom*, 25 (2010) 1704.

23 Caland L B, Silveira E L C & Tubino M, Determination of sodium, potassium, calcium and magnesium cations in biodiesel by ion chromatography, *Anal Chim Acta*, 718 (2012) 116.

24 Korn M G A, Santos D C M B, Guida M A B, Barbosa I S, Passos M L C, Saraiva M L M F S & Lima J L F C, Evaluation of digestion procedures for simultaneous determination of Ca, P, Mg, K and Na in biodiesel by inductively coupled plasma optical emission pectrometry, *J Braz Chem Soc*, 21 (2010) 2278.

25 Jesus A, Silva M M & Vale M G R, The use of microemulsion for determination of sodium and potassium in biodiesel by flame atomic absorption spectrometry, *Talanta*, 74 (2008) 1378.

26 Liu R, Wu P, Xu K, Lv Y & Hou X, Highly sensitive and interference-free determination of bismuth in environmental samples by electrothermal vaporization atomic fluorescence spectrometry after hydride trapping on iridium-coated tungsten coil, *Spectrochimica Acta Part B*, 63 (2008) 704.

27 Rekha D, Suvardhan K, J Kumar D, Subramanyam P, Prasad P R, Lingappa Y & Chiranjeevi P, Solid phase extraction method for the determination of lead, nickel, copper and manganese by flame atomic absorption spectrometry using sodium bispiperdine-1,1'-carbotetrathioate (Na-BPCTT) in water samples, *J Hazard Mater*, 146 (2007) 131.

28 Soylaka M, Tuzen M, Souza A S, Korn M G A & Ferreira S L C, Optimization of microwave assisted digestion procedure for the determination of zinc, copper and nickel in tea samples employing flame atomic absorption spectrometry, *J Hazard Mater*, 149 (2007) 264.

29 Dadfarnia S, Shabani A M H, Bidabadi M S & Jafari A A, A novel ionic liquid/micro-volume back extraction procedure combined with flame atomic absorption spectrometry for determination of trace nickel in samples of nutritional interest, *J Hazardous Mater*, 173 (2010) 534.

30 Lemos V A, Franc R S & Moreira B O, Cloud point extraction for Co and Ni determination in water samples by flame atomic absorption spectrometry, *Sep Purif Technol*, 54 (2007) 349.

31 Mohammadi S Z, Afzali D & Baghelani M, Flame atomic absorption spectrometry determination of trace amounts of nickel ions in water samples after ligandless ultrasound-assisted emulsification microextraction, *Anal Sci*, 26 (2010) 973.

32 Zhou Q X, Zhao X N & Xiao J P, Preconcentration of nickel and cadmium by TiO_2 nanotubes as solid-phase extraction adsorbents coupled with flame atomic absorption spectrometry, *Talanta*, 77 (2009) 1774.

33 Elkady E F, Fouad M A & Mozayad A N, Application of Box-Behnken experimental design and response surface methodology for selecting the optimum RP-HPLC conditions for the simultaneous determination of methocarbamol, indomethacin and betamethasone in their pharmaceutical dosage form, *BMC Chem*, 16 (2022) 114.

34 Ebrahimzadeh H, Tavassoli N, Sadeghi O & Amini M M, Optimization of solid-phase extraction using artificial neural networks and response surface methodology in combination with experimental design for determination of gold by atomic absorption spectrometry in industrial wastewater samples, *Talanta*, 97 (2012) 211.

35 Trawczynska I & Kwiatkowska-Marks S, Application of response surface methodology for optimization of the biosorption process from copper-containing wastewater, *Molecules*, 28 (2023) 444.

36 Alam P, Noman O M, Herqash R N, Almarfadi O M, Akhtar A & Alqahtani A S, Efficient extraction of an anthraquinone physcion using response surface methodology (RSM) optimized ultrasound-assisted extraction method from aerial parts of senna occidentalis and analysis by HPLC-UV, *Separations*, 9 (2022) 142.

37 Minitab 1, Minitab statistical software version 17. State College, Pennsylvania, Minitab, sd, (2014).